

2303 m2 CP

MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO)

19 Apr 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-AB-2001-103**
Jerry Boatz; Don Thompson and Dan Sorescu (Oklahoma State Univ.), "Bond Dissociation Energies of
Energetic Compounds: A Comparison of Theoretical Methods"

AFOSR Contractors Meeting
(Irvine, CA, 21-23 May 2001) (Deadline: 18 May 01)

(Statement A)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.

Comments: _____

Signature _____ Date _____

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Signature _____ Date _____

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Comments: _____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

PHILIP A. KESSEL
Technical Advisor
Space and Missile Propulsion Division

Date



Bond Dissociation Energies of Energetic Compounds: A Comparison of Theoretical Methods

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**AFOSR Molecular Dynamics/Theoretical Chemistry Contractors Conference
May 21-23, 2001
Irvine, CA**



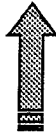
Outline

- I. Overview of AFRL - Propulsion Directorate
 - High Energy Density Materials (HEDM) for rocket propulsion
 - Specific impulse as an assessment of energy density
- II. C-N bond energies of 1,1-diamino-2,2-dinitroethylene ("FOX-7") and prototypes
- III. Results
- IV. Summary and Conclusions



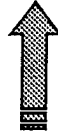
Why is the Air Force interested in HEDM?

The performance limits of current propellants have been reached

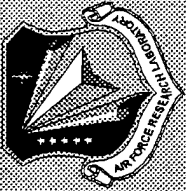


- The constituents of current propellants have been known for decades
- New missions require higher-performing propulsion systems

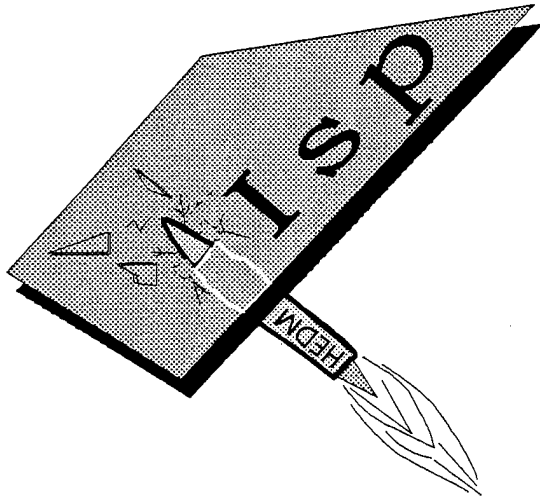
A revolutionary propulsion source would substantially improve our ability to access and exploit space



- Fusion, antimatter, and beamed energy are tantalizing but distant prospects
- Chemical propulsion will remain the method of choice for many applications
- Novel chemical propellants offer great potential for near-term improvements



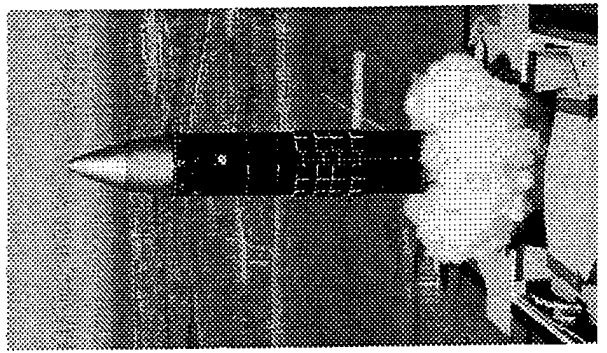
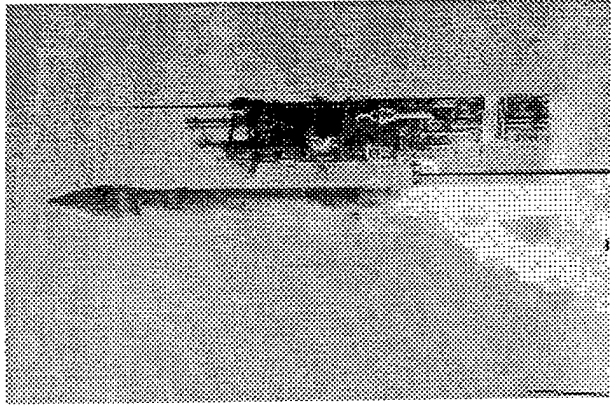
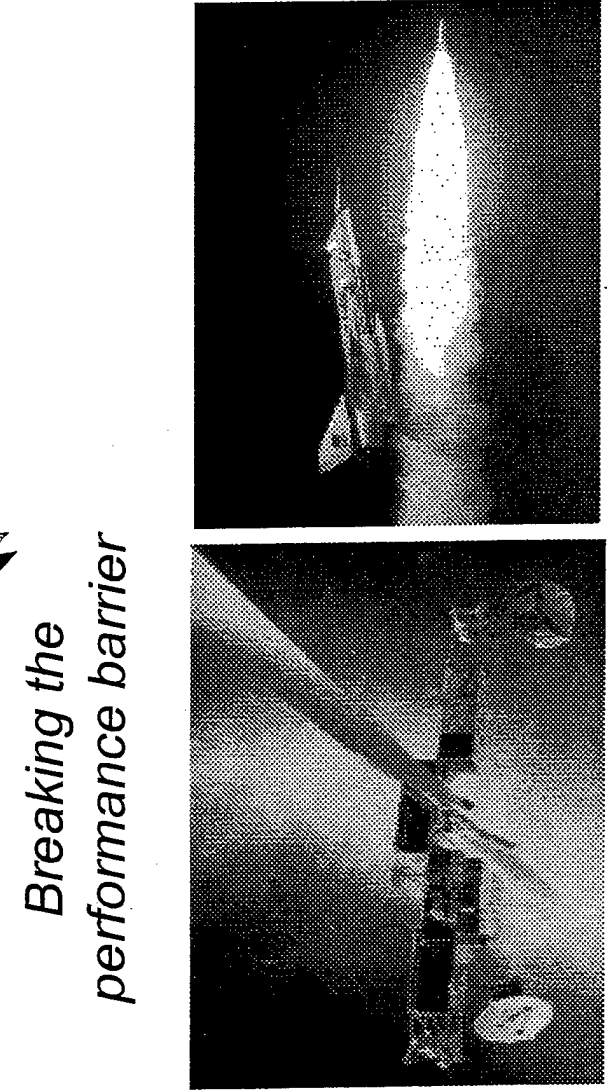
HEDM Program Objective



*Breaking the
performance barrier*

Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for upper stages and satellites
- Cryogenic propellants for upper stages





Assessment of energy density: Specific Impulse (I_{sp})

I_{sp} = pounds of delivered thrust / (pounds of propellant burned/second); similar to mpg.

$$I_{sp} \propto \sqrt{\frac{\Delta H_{comb}}{m_{products}}}$$

=> highly exothermic reactions AND combustion products with small masses are required
(\approx 50% of liquid H_2 in SSME is not burned!)



Specific impulse values of currently used propellants

Solid propellant: Ammonium perchlorate(AP)/Al
powder/hydroxy-terminated polybutadiene (HTPB)

$$I_{sp} = 267 \text{ sec}$$

Liquid propellant: RP-1/LOX

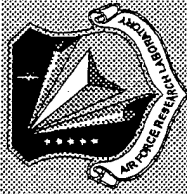
$$I_{sp} = 300 \text{ sec}$$

Monopropellant: Hydrazine (N_2H_4)

$$I_{sp} = 230 \text{ sec}$$

Cryogenic propellants: LH_2/LOX

$$I_{sp} = 390 \text{ sec}$$



HEDM Propellant Payoffs

- Larger payloads, smaller vehicles, and lower launch costs
- Greater capability to access and exploit space

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 (+25%)
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 (+70%)
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/AI/HMX (Isp = 270 s)	1,847	74	110 (+49%)

Our research is aimed at increasing propellant Isp by 5 to 50%



Computational chemistry plays an important role in identification and characterization of HEDM

Experimental synthesis and characterization is difficult

- Little or no intuition to guide synthesis of new molecules.
- Energetic compounds are thermodynamically (and often kinetically) unstable.
- Synthesis is time-consuming, expensive, high-risk.



Energetic compounds present several challenges to theory

Exotic electronic structures

- Large non-dynamical correlation effects => single configuration methods may not be applicable.
- Multiple potential energy surfaces (e.g., low-lying triplet state(s) often intersect the lowest singlet state.)
- Nonadiabatic interactions (e.g., spin-orbit coupling, radiationless transitions)



Which theoretical method(s) give reliable predictions?

Density Functional Theory

- Widely used due to its efficiency and accuracy (generally comparable to MP2.)

Single-configuration correlated methods

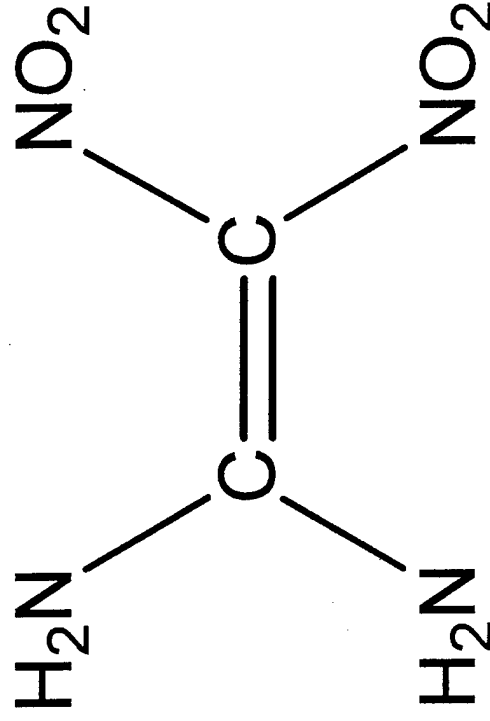
- MPn, CC, QCI, G2

Multiconfigurational methods

- MCSCF, MCQDPT, MRCI, MRCC



FOX-7: A prototypical energetic compound



$I_{sp} = 254$ sec (calculated)
 $\Delta H_f = -9.5$ kcal/mol (G2(MP2))

Advantages:

- Chemically balanced wrt decomposition products ($2CO + 2H_2O + 2N_2$)
- Lower impact/shock sensitivity than other $C_nH_{2n}O_{2n}N_{2n}$ compounds (e.g., RDX and HMX).



Recent Studies of FOX-7

Experimental X-ray structure

U. Bemm and H. Östmark, Acta Cryst. C54, 1997(1998).

Structures and C-N bond energies (B3P86/6-31+G(d,p))

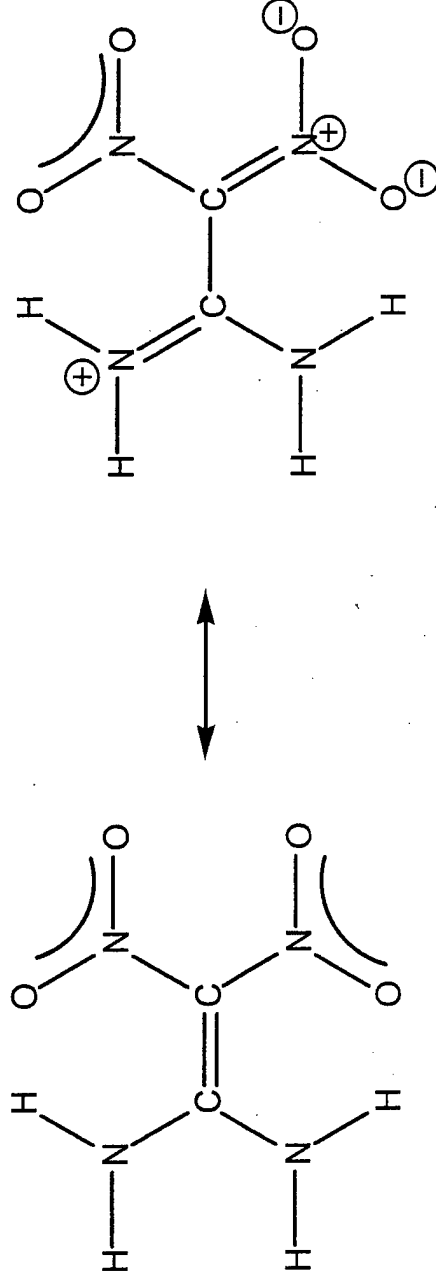
P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and
D.Habibollazadeh Theochem, 452, 75(1998)

Decomposition mechanisms (B3P86/6-31+G(d,p), B3LYP/6-31+G(d,p))

A.Gindulyte, L.Massa, L.Huang, and J.Karl, J. Phys. Chem. A, 103,
11045(1999)



FOX-7: A “Push-Pull” Ethylene

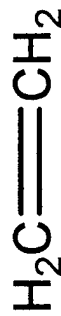


Multiple Lewis structures suggest that FOX-7 may have high degree of multiconfigurational character
=> good testbed for SOTA single-reference methods and DFT.

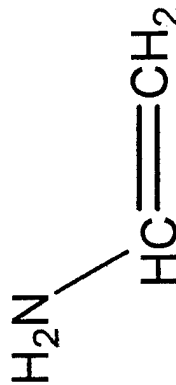
DFT Geometries

C=C C-NH₂ C-NO₂

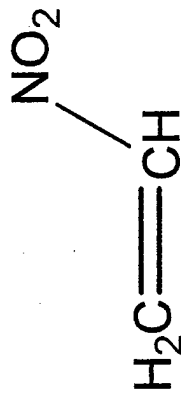
1.331*
1.327



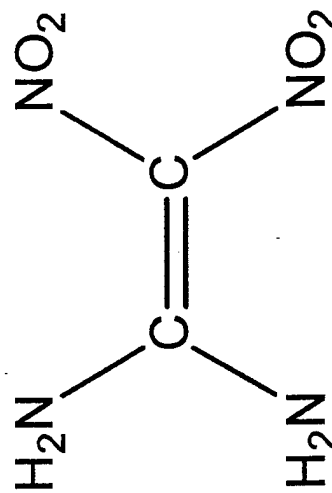
1.340* 1.386*
1.336 1.392



1.326* 1.459*
1.322 1.473



1.426* 1.339* 1.424*
1.428** 1.345** 1.432**
1.421 1.345 1.438
(1.456) (1.319, 1.325) (1.399, 1.426)



* P. Politzer, M.C. Concha, M.E. Grice, J.S. Murray, P. Lane, and D. Habibollahzadeh
Theochem, 452, 75(1998)

** A. Gindulyte, L. Massa, L. Huang, and J. Karl, J. Phys. Chem. A, 103, 11045(1999)

() U. Bemm and H. Östmark, Acta Cryst. C54, 1997(1998).



Approach

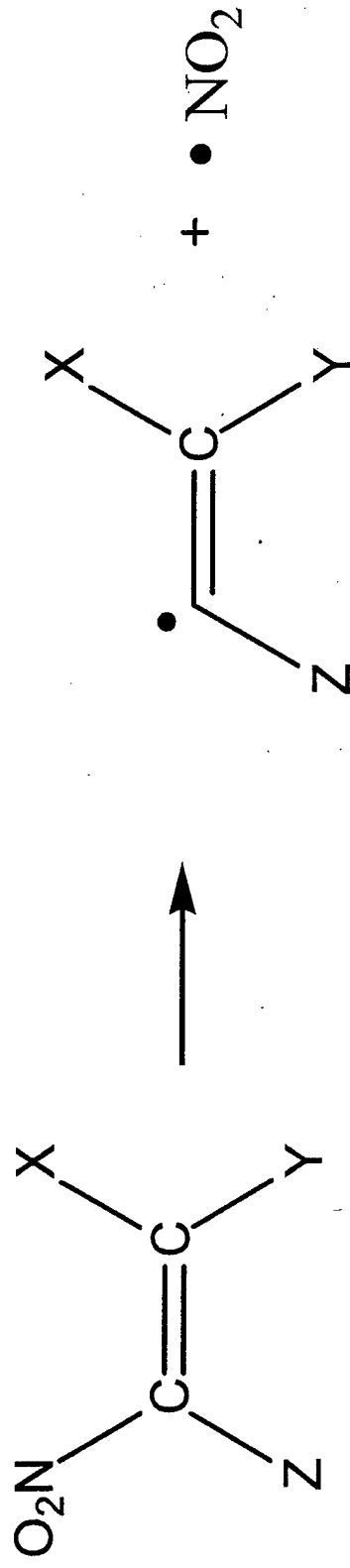
1. Compute C-NH₂ and C-NO₂ bond dissociation energies of FOX-7 and simpler prototypes using DFT (B3LYP), single-reference methods (MP2, G2(MP2), CCSDT//MP2), and a multireference method (MCQDPT(2)//CASSCF). 6-311G(d,p) used throughout.
2. Assess degree of multiconfigurational character via calculation of natural orbital occupation numbers (MP2, CCSD(T), MCSCF).

- MP2 and CCSD(T) “non-physical” occupation numbers indicative of significant degree of multiconfigurational character

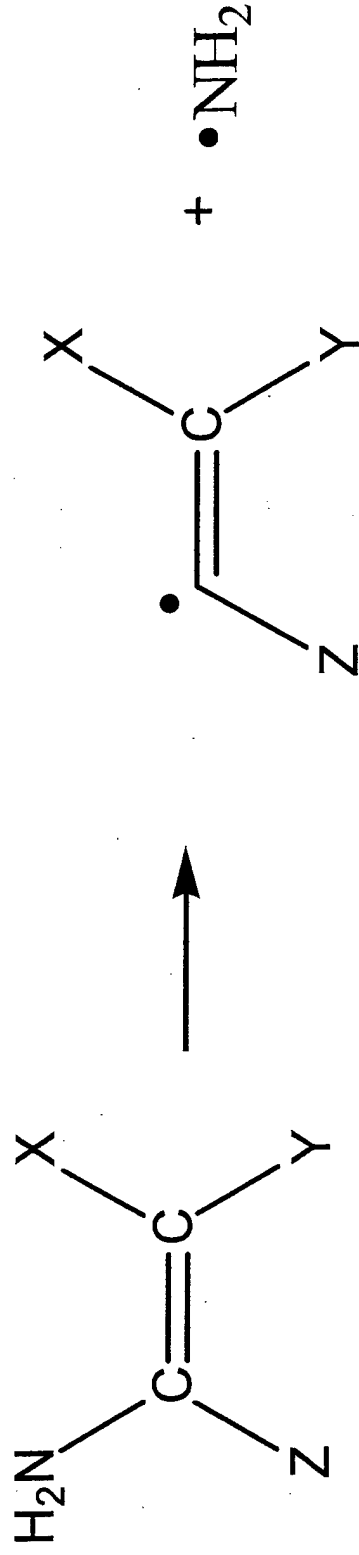
M.S. Gordon, M.W. Schmidt, G.M. Chaban, K. R. Glaesemann, W.J. Stevens, and C. Gonzalez, J. Chem. Phys., 110, 4199 (1999).

Bond Dissociation Reactions

C-NO₂ BDEs: X, Y = H, NH₂ ; Z = H, NO₂



C-NH₂ BDEs: X, Y = H, NO₂ ; Z = H, NH₂



Choice of CASSCF Active Space

“Push-pull” Lewis structures suggest that delocalization of π electrons account for the most important non-dynamical correlation.



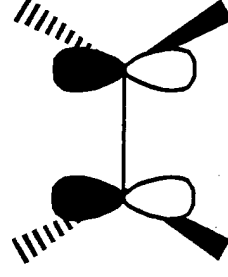
π



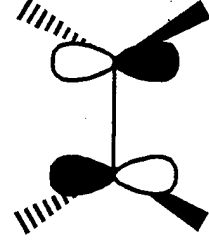
non-bonding



π^*



π



π^*

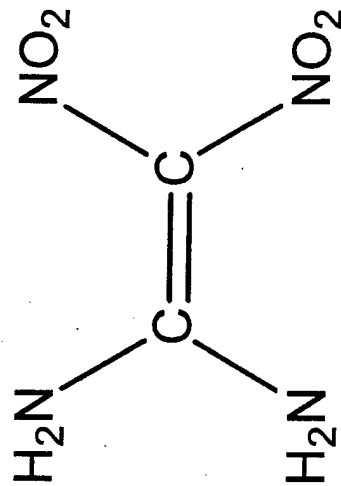


σ



σ^*

Structures of FOX-7



* P. Politzer, M.C. Concha, M.E. Grice, J.S. Murray, P. Lane, and D. Habibollahzadeh Theochem, 452, 75(1998)

** A. Gindulyte, L. Massa, L. Huang, and J. Karl, J. Phys. Chem. A, 103, 11045(1999)

() U. Bemm and H. Östmark, Acta Cryst. C54, 1997(1998).

Level of theory

B3P86/6-31+G(d,p)

B3LYP/6-31+G(d,p)

B3LYP/6-311G(d,p)

MP2/6-311G(d,p)

CASSCF/6-311G(d,p)

C=C

1.426*

1.428**

1.421

1.392

C-NH₂

1.339*

1.345**

1.345

1.359

C-NO₂

1.424*

1.432**

1.438

1.441

X-ray structure

(1.456)

(1.319)

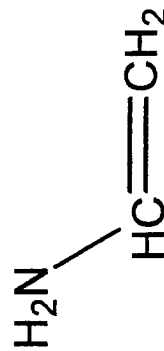
(1.325)

(1.399)

(1.426)

Natural Orbital Occupation Numbers

(closed shell species)

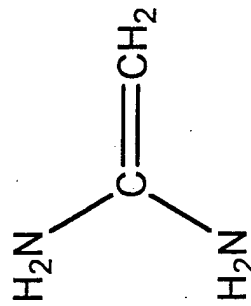


MP2: none

CCSD(T): none

<----- MCSCF (6e,5o) ----->

C=C	π	π^*
	1.927	0.079
C-NH ₂	σ	σ^*
	1.980	0.020
NH ₂ lp	1.994	



MP2: -0.001

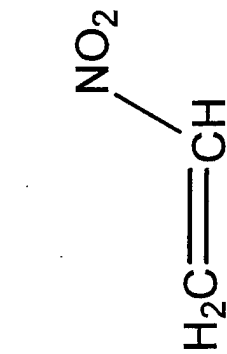
CCSD(T): none

<----- MCSCF (8e,7o) ----->

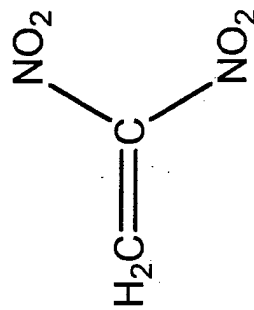
C=C	π	π^*
	1.940	0.068
C-NH ₂	σ	σ^*
	1.978	0.023
	1.981	0.019
NH ₂ lp	1.995	

Natural Orbital Occupation Numbers

(closed shell species)



MP2: 2.00001,
-0.00009
CCSD(T): none



MP2: -0.001
CCSD(T): none

<----- MCSCF (8e,7o) ----->

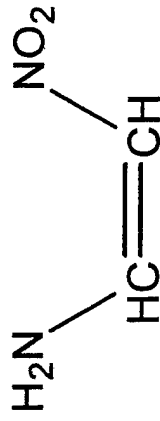
C=C	π	π*	
	1.914	0.077	
NO ₂	π	n.b.	π*
	1.983	1.897	0.130
C-NO ₂	σ	σ*	
	1.977	0.023	

<----- MCSCF (14e,12o) ----->

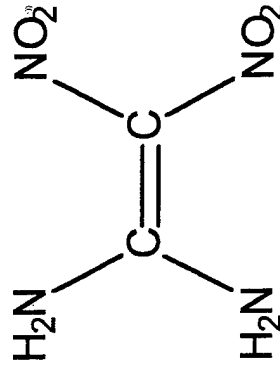
C=C	π	π*	
	1.915	0.077	
NO ₂	π	n.b.	π*
	1.984	1.889	0.132
	1.984	1.883	0.137
C-NO ₂	σ	σ*	
	1.977	0.030	
	1.973	0.020	

Natural Orbital Occupation Numbers

(closed shell species)



MP2: -0.00001(2)
CCSD(T): none



MP2: 2.00001(3),
-0.00016, -0.00009,
-0.00004, -0.00001
CCSD(T): none

<----- MCSCF (12e,10o) ----->

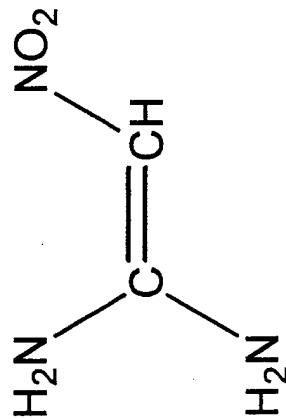
C=C	π	π*	
	1.950	0.059	
NO ₂	π	n.b.	π*
	1.983	1.914	0.108
C-NH ₂	σ	σ*	
	1.981	0.019	
C-NO ₂	σ	σ*	
	1.978	0.023	
NH ₂ lp	1.987		

<----- MCSCF (18e,14o) ----->

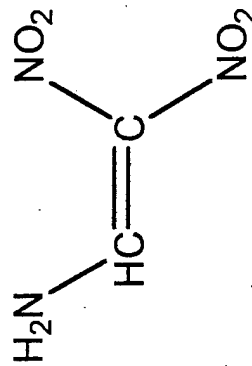
C=C	π	π*	
	1.983	0.036	
NO ₂	π	n.b.	π*
	1.986	1.911	0.099
	1.989	1.906	0.113
C-NH ₂	σ	σ*	
	1.982	0.018	
	1.978	0.022	
C-NO ₂	σ	σ*	
	----- n/a -----		
NH ₂ lp	1.988(2)		

Natural Orbital Occupation Numbers

(closed shell species)



MP2: -0.0001(2)
CCSD(T): none



MP2: -0.0002(2),
-0.00001
CCSD(T): none

<----- MCSCF (16e,13o) ----->

C=C	π	π^*	
	1.962	0.050	
NO ₂	π	n.b.	π^*
	1.983	1.921	0.100
C-NH ₂	σ	σ^*	
	1.982	0.018	
	1.977	0.022	
C-NO ₂	σ	σ^*	
	1.979	0.024	
NH ₂ lp	1.994		
	1.990		

<----- MCSCF (18e,15o) ----->

C=C	π	π^*	
		TBD	
NO ₂	π	n.b.	π^*
		TBD	
C-NH ₂	σ	σ^*	
		TBD	
C-NO ₂	σ	σ^*	
		TBD	
NH ₂ lp		TBD	

Natural Orbital Occupation Numbers

(open shell species)



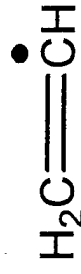
MP2: none
CCSD(T): none

<----- MCSCF (3e,2o) ----->
NH₂ lp 2.000
N rad. 1.000



MP2: 2.00001
CCSD(T): none

<----- MCSCF (5e,4o) ----->
NO₂ π n.b. π*
1.986 1.937 0.078
N rad. 1.000



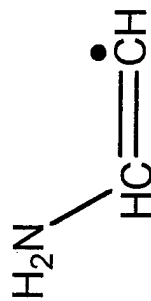
MP2: 2.07575,
-0.08353

CCSD(T): none

<----- MCSCF ----->
C=C π π*
1.899 0.101
C rad. 1.000

Natural Orbital Occupation Numbers

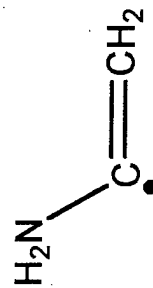
(open shell species)



MP2: 2.06629,

-0.08353

CCSD(T): none



MP2: TBD

CCSD(T): TBD

<----- MCSCF (7e,6o) ----->

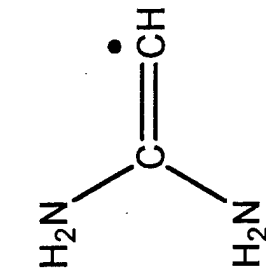
C=C	π	π^*	
	1.911	0.094	
C-NH ₂	σ	σ^*	
	1.980	0.021	
NH ₂ lp	1.995		
C rad.	1.000		

<----- MCSCF (7e,6o) ----->

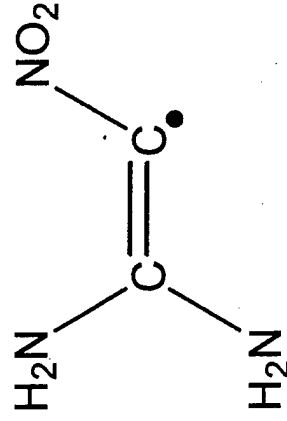
C=C	π	π^*	
	1.918	0.084	
C-NH ₂	σ	σ^*	
	1.981	0.019	
NH ₂ lp	1.993		
C rad.	1.006		

Natural Orbital Occupation Numbers

(open shell species)



MP2: 2.04703,
2.00001, -0.06203,
-0.00003
CCSD(T): none



MP2: TBD
CCSD(T): TBD

<----- MCSCF (11e,9o) ----->

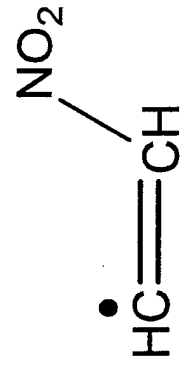
C=C	π	π^*
	1.924	0.083
C-NH ₂	σ	σ^*
	1.977	0.023
	1.980	0.020
NH ₂ lp	1.994	
	1.997	
C rad.	1.001	

<----- MCSCF (13e,12o) ----->

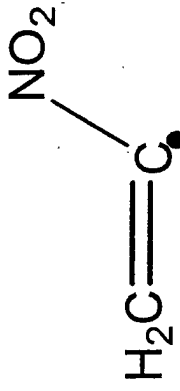
C=C	π	π^*
	1.929	0.068
NO ₂	π	n.b. π^*
	1.9834	1.907 0.114
C-NH ₂	σ	σ^*
	1.982	0.017
	1.980	0.020
C-NO ₂	σ	σ^*
	1.977	0.024
NH ₂ lp	---	n/a ---

Natural Orbital Occupation Numbers

(open shell species)



MP2: 2.08805,
2.00001, -0.00001,
-0.00006
CCSD(T): none



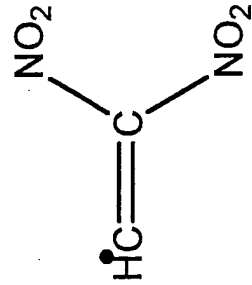
MP2: 2.09302,
2.00001, -0.00008,
-0.10792
CCSD(T): TBD

<----- MCSCF (9e,8o) ----->			
C=C	π	π^*	
	1.904	0.083	
NO ₂	π	n.b.	π^*
	1.983	1.900	0.134
C-NO ₂	σ	σ^*	
	1.975	0.025	
C rad.	1.000		

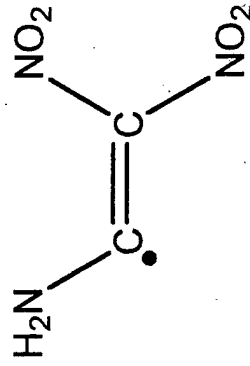
<----- MCSCF (9e,8o) ----->			
C=C	π	π^*	
	1.896	0.090	
NO ₂	π	n.b.	π^*
	1.983	1.891	0.141
C-NO ₂	σ	σ^*	
	1.977	0.023	
C rad.	1.000		

Natural Orbital Occupation Numbers

(open shell species)



MP2: 2.08603,
2.00001(2),
-0.10207, -0.00003
CCSD(T): TBD



MP2: 2.00001(2),
-0.0013, -0.00055
CCSD(T): none

<----- MCSCF (15e,13o) ----->

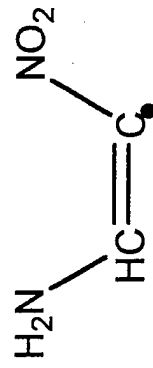
C=C	π	π^*	
	1.904	0.084	
NO ₂	π	n.b.	π^*
	1.984	1.882	0.142
	1.984	1.888	0.133
C-NO ₂	σ	σ^*	
	1.972	0.031	
	1.976	0.021	
C rad.		1.000	

<----- MCSCF (15e,12o) ----->

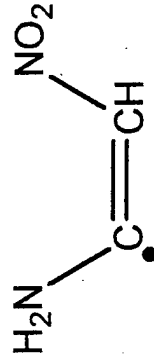
C=C	π	π^*	
	1.976	0.043	
NO ₂	π	n.b.	π^*
	1.989	1.905	0.114
	1.987	1.909	0.103
C-NO ₂	σ	σ^*	
	----- n/a -----		
C-NH ₂	σ	σ^*	
	1.981	0.020	
NH ₂ lp		1.974	
C rad.		1.000	

Natural Orbital Occupation Numbers

(open shell species)



MP2: 2.05145,
2.00001, -0.00014,
-0.06755
CCSD(T): TBD



MP2: 2.00001,
-0.00002, -0.00015,
-0.01124
CCSD(T): TBD

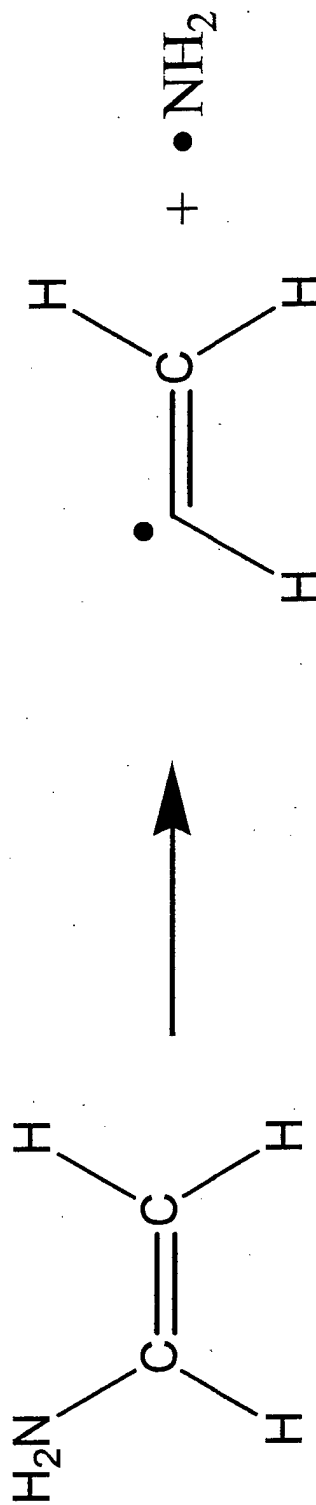
<----- MCSCF (13e,11o) ----->

C=C	π	π^*	
	1.923	0.079	
NO ₂	π	n.b.	π^*
	1.983	1.906	0.119
C-NO ₂	σ	σ^*	
	1.977	0.024	
C-NH ₂	σ	σ^*	
	1.979	0.019	
NH ₂ lp	1.990		
C rad.	1.001		

<----- MCSCF (13e,11o) ----->

C=C	π	π^*	
	1.938	0.064	
NO ₂	π	n.b.	π^*
	1.982	1.911	0.112
C-NO ₂	σ	σ^*	
	1.976	0.025	
C-NH ₂	σ	σ^*	
	1.980	0.019	
NH ₂ lp	1.987		
C rad.	1.006		

C-NH₂ Bond Dissociation Energies (kcal/mol)



DFT	105.2
	109.8 (103.3)*
MBPT(2)	115.6
G2(MP2)	110.8 (102.4)
CCSD(T)//MBPT(2)	104.7
MCQDPT(2)//MCSCF	101.9
experiment [†]	102

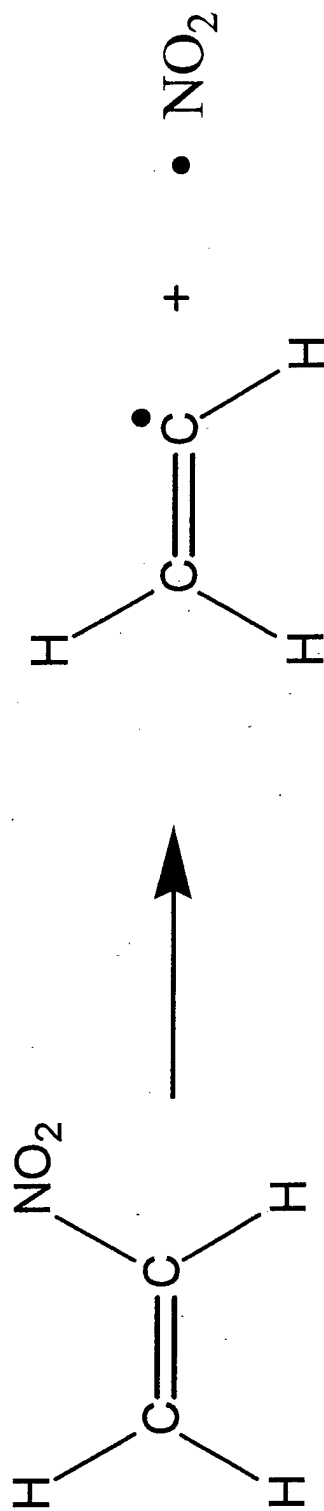
----- Non-physical NOONS -----	•NH ₂	----- MCSCF -----
MBPT(2)	CCSD(T)	
none	none	n/a
----- Non-physical NOONS -----	•CH=CH ₂	----- MCSCF(3e,3o) -----
MBPT(2)	CCSD(T)	C=C π π*
2.07575	none	1.899 0.101
-0.09409		C rad. 1.000

----- Non-physical NOONS -----	NH ₂ CH=CH ₂	----- MCSCF(6e,5o) -----
MBPT(2)	CCSD(T)	C=C π π*
none	none	1.927 0.079
		NH ₂ Ip 1.994
		C-NH ₂ σ σ*
		1.980 0.020

* P. Politzer, M.C. Concha, M.E. Grice, J.S. Murray, P. Lane, and D. Habibollahzadeh Theochem, 452, 75(1998). Values in () include ZPE corrections.

† S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1), 1988.

C-NO₂ Bond Dissociation Energies (kcal/mol)



DFT	68.8
	74.5*
MBPT(2)	77.7
G2(MP2) [†]	79.4
CCSD(T)//MBPT2	70.9
MCQDPT(2)//MCSCF	59.5

----- Non-physical NOONS -----	•NO ₂	----- MCSCF(5e,4o) -----
MBPT(2) CCSD(T)	NO ₂ π n.b.	π* π*
2.00001 none	1.986 1.937	0.078
	N rad.	1.000

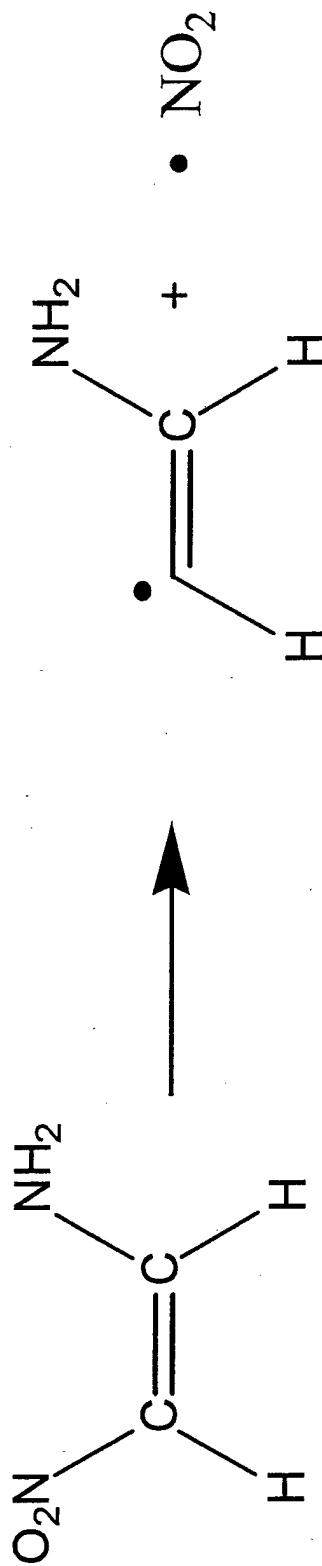
----- Non-physical NOONS -----	•CH=CH ₂	----- MCSCF(3e,3o) -----
MBPT(2) CCSD(T)	C=C π	π* π*
2.07575 none	1.899	0.101
-0.09409	C rad.	1.000

----- Non-physical NOONS -----	NO ₂ CH=CH ₂	----- MCSCF(8e,7o) -----
MBPT(2) CCSD(T)	C=C π	π* π*
2.00001 none	1.914	0.077
-0.00009	NO ₂ π n.b.	π* π*
-0.00004	1.983 1.897	0.130
	C-NO ₂ σ σ*	1.977 0.023

* P. Politzer, M.C. Concha, M.E. Grice, J.S. Murray, P. Lane, and D. Habibollahzadeh Theochem, 452, 75(1998).

[†] Does not include ZPE corrections.

C-NO₂ Bond Dissociation Energies (kcal/mol)



DFT

81.4

MBPT(2)

86.2

G2(MP2)[†]

88.8

CCSD(T)//MBPT2

78.2

MCQDPT(2)//MCSCF

66.7

•NO₂

----- Non-physical NOONS -----

----- MCSCF(5e,4o) -----

MBPT(2) CCSD(T)

NO₂ π n.b. π*

2.00001 none

1.986 1.937 0.078

N rad. 1.000

•CH=CH-NH₂

----- Non-physical NOONS -----

----- MCSCF(7e,6o) -----

MBPT(2) CCSD(T)

C=C π π*

2.06629 none

1.911 0.094

-0.08353

C rad. 1.000

-0.00001

NH₂ lp 1.995

* P. Politzer, M.C. Concha, M.E. Grice, J.S. Murray, P. Lane, and D. Habibollahzadeh Theochem, 452, 75(1998).

[†] Does not include ZPE corrections.

NO₂CH=CH-NH₂

----- Non-physical NOONS -----

----- MCSCF(12e,10o) -----

MBPT(2) CCSD(T)

C=C π π*

2.00001 TBD

1.950 0.059

-0.00009

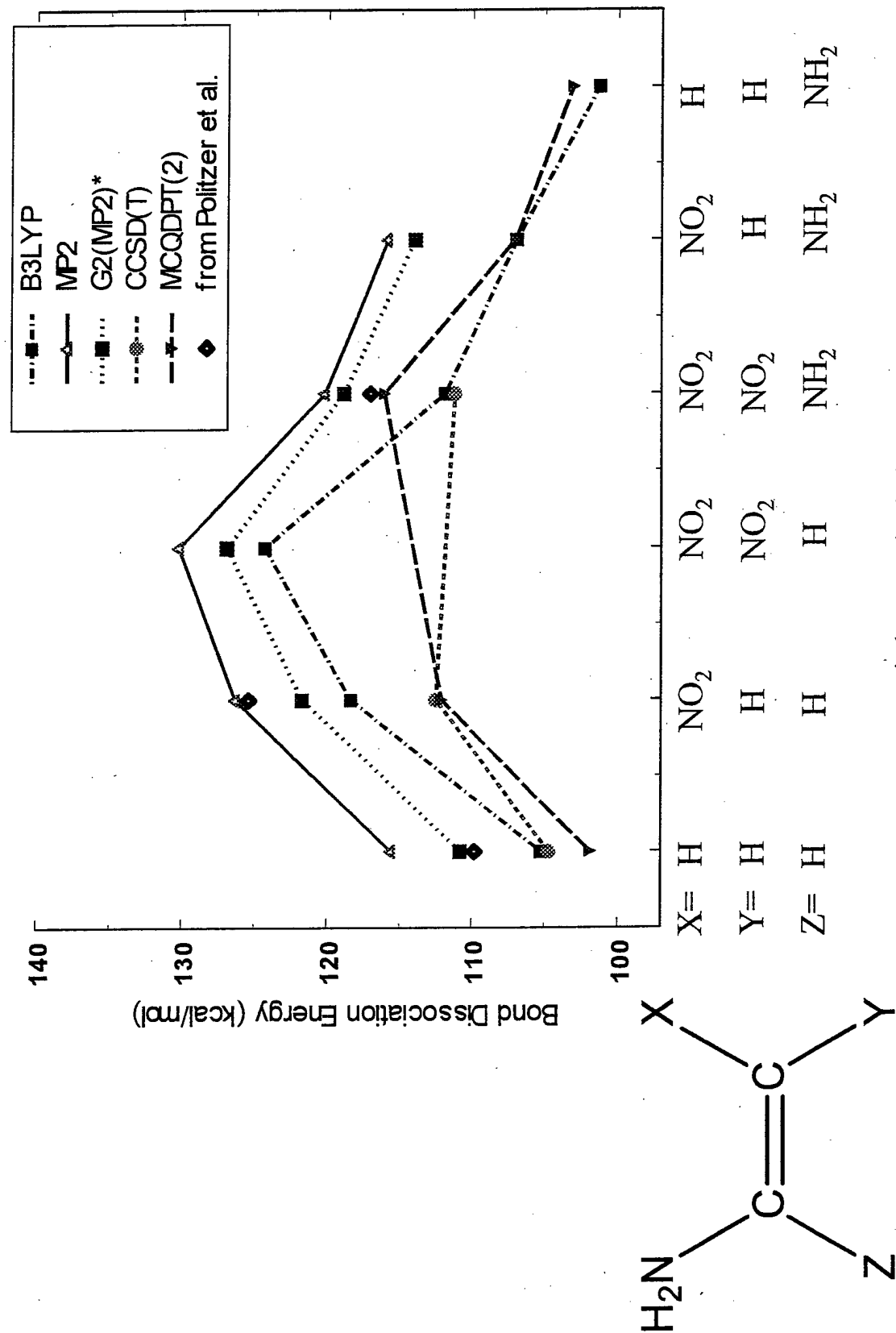
NO₂ π n.b. π*

-0.00004

1.983 1.914 0.108

NH₂ lp 1.987

C-NH₂ Bond Dissociation Energies (kcal/mol)



* does not include ZPE corrections



Summary and Conclusions

1. The C-NH₂ and C-NO₂ bond dissociation energies of FOX-7 and simpler prototypes have been computed using DFT (B3LYP), single-reference (SR) methods (MP2, G2(MP2), CCSD(T)//MP2), and a multireference (MR) method (MCQDPT(2)//CASSCF).
2. With the exception of aminoethylene and amino radical, all of the closed shell and radical species considered in this study have non-physical NOONs at the MP2 level.
3. CCSD(T) is better able to "capture" non-dynamical correlation than MP2.
4. Species containing a nitro group generally have a higher degree of multiconfigurational character than those without NO₂.
5. The DFT BDEs generally are in better agreement with the SR methods (MP2, G2(MP2), CCSD(T)) than with MCQDPT(2)), particularly for C-NO₂.
6. The MCQDPT(2) BDEs are lower than those of the SR methods. The difference between the SR and MR predictions is greater for C-NO₂ than C-NH₂.
7. The most stringent comparison of these methods will likely be the C-NO₂ BDE for (NH₂)₂C=C(NO₂)₂, for which the radical (NH₂)₂C=C-NO₂ is exceptionally MR in nature.



Future Directions

1. Include additional MR methods (MRCI, MRCC).
2. For the smaller systems, try larger basis sets (cc-pVTZ).
3. Replace UHF reference with ROHF for MP2, CCSD(T).

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